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KNOCK-LIMITED PERFORMANCE OF BLENDS OF AN-F-28 FUEL

CONTAINING 2 PERCENT AROMATIC AMINES - V

By Henry Alquist and Leonard K. Tower

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NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

MEMORANDUM REPORT

for the

Air Technical Service Command, Army Air Forces

KNOCK-LIMITED PERFORMANCE OF BLENDS OF AN-F-28 FUEL

CONTAINING 2 PERCENT AROMATIC AMINES - V

By Henry Alquist and Leonard K. Tower

SUMMARY

Tests were conducted to determine the effect of 2-percent additions of seven aromatic amines on the knock-limited performance of 28-R fuel in a CFR engine. Knock tests were made of seven aromatic amines synthesized, or purchased and purified, at the Cleveland laboratory of the NACA. The amines tested were N-methyl-p-ethylaniline, N-methyl-o-toluidine, N-methyl-p-isopropylaniline, N-methyl-2,4-xylidine, methyldiphenylamine, N-methyl-ar-ethylaniline (mixture of N-methyl ethylanilines), and 2,4,6-trimethylaniline. The knock-limited performance of 28-R fuel with and without 2-percent additions of each of these aromatic amines was determined with a modified F-4 engine at three sets of operating conditions. Ratings were also determined for 28-R and all the fuel blends with an F-3 engine.

The results are summarized as follows:

1. The most effective antiknock additives of the aromatic amines tested were N-methyl-ar-ethylaniline, N-methyl-p-ethylaniline, and N-methyl-p-isopropylaniline.
2. Other aromatic amines which are of interest as antiknock additives are N-methyl-2,4-xylidine, N-methyl-o-toluidine, and 2,4,6-trimethylaniline.
3. With certain exceptions the addition of a single methyl radical to the nitrogen atom of an aromatic amine increased the knock-limited power and decreased the temperature sensitivity at most fuel-air ratios and engine conditions.

## INTRODUCTION

A general program is being conducted at the Cleveland laboratory of the NACA at the request of the Air Technical Service Command, Army Air Forces, to determine the effectiveness of aromatic amines as antiknock additives in aviation fuel. This report is the last of a series of five reports presenting knock data on a total of 48 aromatic amines. (See references 1 to 4.) Six of the aromatic amines were tested as technical mixtures in a full-scale aircraft cylinder and the knock-limited performance data of these amines is discussed in reference 5. The preignition-limited performance of 2-percent additions of six of the aromatic amines is discussed in reference 6. The low-temperature solubility of the amines and the suitability for overwater storage of their gasoline blends are presented in references 7 to 9.

The present paper reports knock-limited performance data, obtained during March 1945, for seven aromatic amines. It is emphasized that knock in a CFR engine is the sole criterion for evaluating the amines in this series.

## APPARATUS AND TEST PROCEDURE

The seven aromatic amines were distilled through a fractionating column and a narrow fraction (approximately 1° C) in the middle of the boiling range was selected for the engine tests.

Knock tests were performed on a modified F-4 engine with the same operating conditions reported in references 1 to 4. The operating conditions, ranging from severe to mild, are as follows:

	Inlet-air tempera- ture (°F)	Spark advance (deg B.T.C.)	Coolant Tem- perature (°F)
F-4 method	225	45	375
Modification A	250	30	250
Modification B	150	30	250

At each of these sets of conditions 28-R fuel and a 2-percent blend of an aromatic amine in this fuel were tested on the same day.

F-3 ratings for 28-R fuel and for the amine blends were also obtained.

## DISCUSSION OF RESULTS

Figures 1 to 7 present knock-limited performance data for the seven aromatic amines. Each figure compares the effects of the transition from severe to mild test conditions for 28-R fuel and for a 2-percent addition of one aromatic amine to this fuel. Table I summarizes the data presented in figures 1 to 7 at fuel-air ratios of 0.062, 0.070, 0.090, and 0.110. The F-3 ratings of the amines are presented in table II.

The results of previous tests of 41 aromatic amines have indicated that the addition of one N-alkyl radical to the amine results in an increase in knock-limited power. A further indication of this effect can be seen by comparing the data for N-methyl-p-isopropylaniline, N-methyl-o-toluidine, methyldiphenylamine, N-methyl-2,4-xylydine, and N-methyl-p-ethylaniline presented in this report and the data for p-isopropylaniline (reference 1), o-toluidine (reference 2), diphenylamine (reference 3), 2,4-xylydine (reference 3), and p-ethylaniline (reference 4).

The addition of a methyl radical to the nitrogen atom of p-isopropylaniline, o-toluidine, 2,4-xylydine, and p-ethylaniline had similar effects. The knock-limited performance of these monosubstituted amines was raised slightly and the temperature sensitivity somewhat decreased with respect to the corresponding unsubstituted compound at most fuel-air ratios and engine conditions.

Methyldiphenylamine (fig. 5) did little to improve the performance of 28-R fuel whereas a 2-percent addition of diphenylamine in 28-R fuel gave an average knock-limited performance about 10 percent higher than 28-R fuel. (See reference 3.) This difference conforms to a previous observation (reference 3) that the N monosubstituted aniline compounds are better antiknock additives than the corresponding NN' disubstituted compounds.

Among the aromatic amines considered herein, N-methyl-ar-ethyl-aniline (fig. 6), N-methyl-p-isopropylaniline (fig. 3), and N-methyl-p-ethylaniline (fig. 1) permitted the best knock-limited performance; the knock limit of these aromatic amine blends at severe operating conditions was about the same as that of 28-R fuel in the lean region and at a fuel-air ratio of 0.110 was about 15 percent higher than 28-R fuel. Under milder operating conditions there was a considerable gain over 28-R in knock-limited power at all fuel-air ratios.

Blends of 2-percent N-methyl-o-toluidine, N-methyl-2,4-xylydine, and 2,4,6-trimethylaniline with 28-R fuel improved the knock-limited performance of 28-R fuel at the moderate engine conditions and high fuel-air ratios.

## SUMMARY OF RESULTS

The results of the knock-limited performance tests with the modified F-4 engine to determine the antiknock effectiveness of 2-percent additions of seven aromatic amines to 28-R fuel are summarized as follows:

1. The most effective antiknock additives of the aromatic amines tested were N-methyl-ar-ethylaniline, N-methyl-p-ethylaniline, and N-methyl-p-isopropylaniline.

2. Other aromatic amines which are of interest as antiknock additives are N-methyl-2,4-xylydine, N-methyl-o-toluidine, and 2,4,6-trimethylaniline.

3. With certain exceptions the addition of a single methyl radical to the nitrogen atom of an aromatic amine increased the knock-limited power and decreased the temperature sensitivity at most fuel-air ratios and engine conditions.

Aircraft Engine Research Laboratory,  
National Advisory Committee for Aeronautics,  
Cleveland, Ohio, August 6, 1945.

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TABLE I - SUMMARY OF ANTIKNOCK EFFECTIVENESS OF AROMATIC AMINE ADDITIONS TO 28-R FUEL

	Inlet-air temperature (°F)	Coolant temperature (°F)	Spark advance (deg B.T.C.)
F-4 method	225	375	45
Modification A	250	250	30
Modification B	150	250	30

Aromatic amine (2-percent addi- tion to 28-R)	Relative power = $\frac{\text{imep}(\text{aromatic amine plus 28-R})}{\text{imep}(28\text{-R})}$											
	F/A = 0.062			F/A = 0.070			F/A = 0.090			F/A = 0.110		
	F-4 method	Modi- fica- tion A	Modi- fica- tion B	F-4 method	Modi- fica- tion A	Modi- fica- tion B	F-4 method	Modi- fica- tion A	Modi- fica- tion B	F-4 method	Modi- fica- tion A	Modi- fica- tion B
28-R	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
N-Methyl-p-ethyl- aniline	.97	1.14	1.13	.98	1.18	1.16	1.06	1.14	1.12	1.14	1.15	1.13
N-Methyl-o-toluidine	.97	1.07	1.08	.95	1.07	1.07	.95	1.10	1.09	1.02	1.11	1.14
N-Methyl-p-isopropyl- aniline	.95	1.15	1.11	1.05	1.17	1.14	1.08	1.14	1.12	1.15	1.11	1.14
N-Methyl-2,4-xylidine	.98	1.07	1.08	1.00	1.08	1.09	1.00	1.09	1.06	1.04	1.15	1.04
Methyldiphenylamine	1.00	1.06	1.16	1.10	1.01	1.04	1.04	1.01	1.00	1.01	1.01	1.07
N-Methyl-ar-ethyl- aniline	1.00	1.18	1.18	1.00	1.20	1.16	1.08	1.16	1.11	1.15	1.12	1.11
2,4,6-Trimethylaniline	.88	1.16	1.06	.92	1.07	1.05	.98	1.08	1.08	1.05	1.10	1.11

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TABLE II - F-3 RATINGS OF 2-PERCENT BLENDS OF  
AROMATIC AMINES AND 28-R FUEL

Aromatic amine (2-percent addition to 28-R fuel)	F-3 rating	
	Octane number, or tetraethyl lead in S-3 reference fuel (ml/gal)	Performance number
28-R	100	100
N-Methyl- <u>p</u> -ethylaniline	100	100
N-Methyl- <u>o</u> -toluidine	100	100
N-Methyl- <u>p</u> -isopropylaniline	0.05	102
N-Methyl-2,4-xylydine	0.03	101
Methyldiphenylamine	0.03	101
N-Methyl- <u>ar</u> -ethylaniline	0.03	101
2,4,6-Trimethylaniline	99.2	97.5

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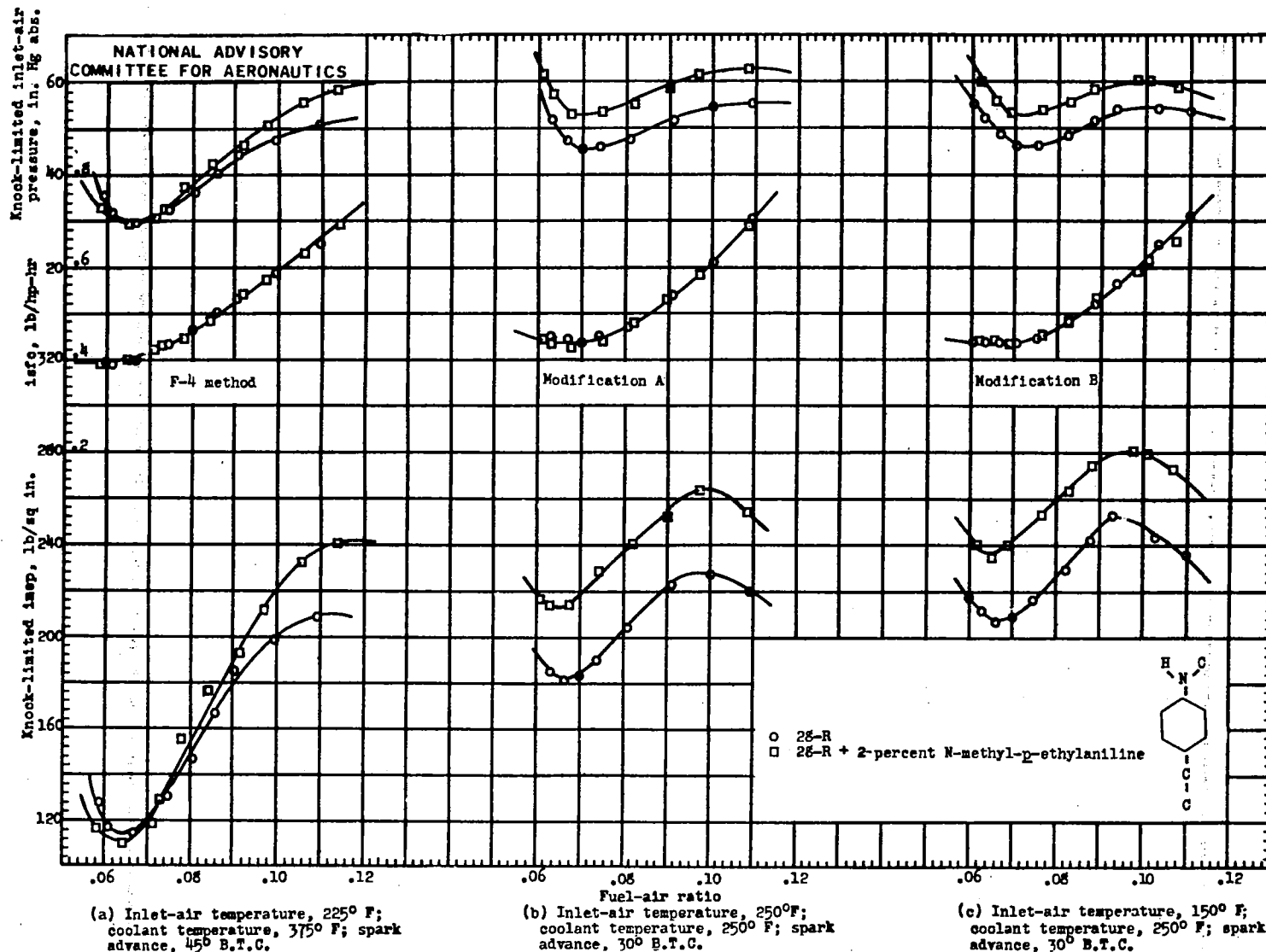


Figure 1. - Effect of addition of 2-percent N-methyl-p-ethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.

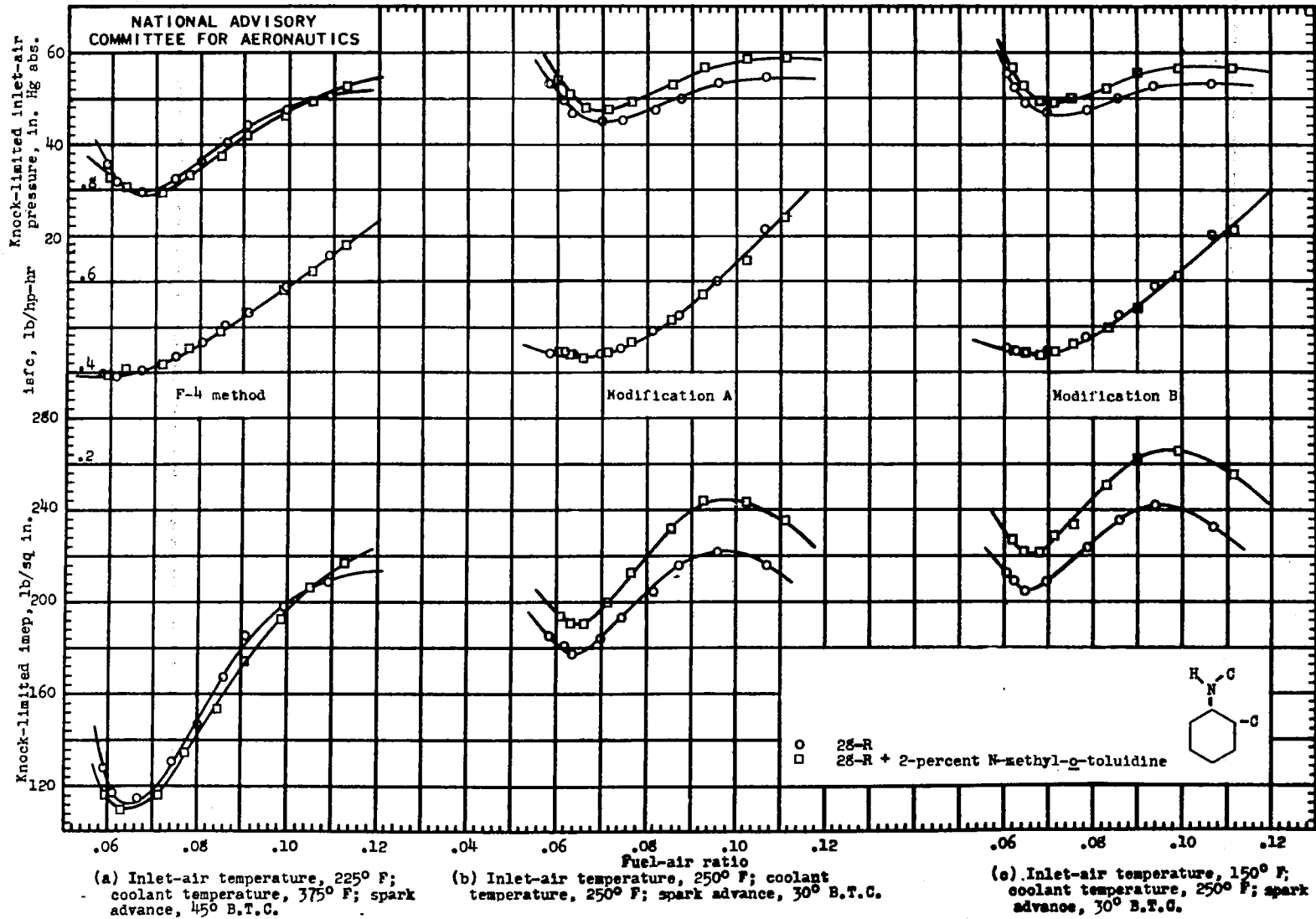


Figure 2. - Effect of addition of 2-percent N-methyl-o-toluidine to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.

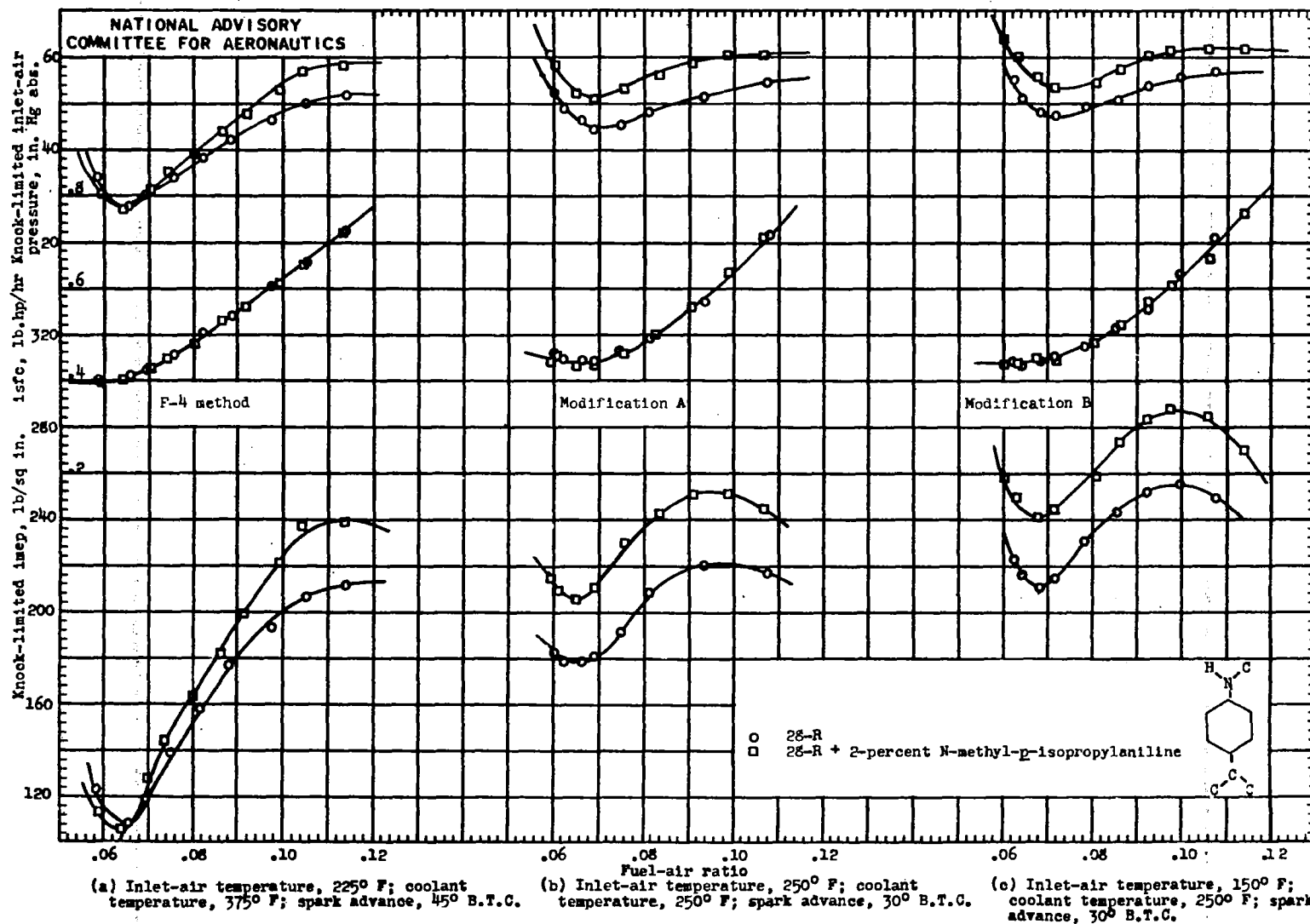
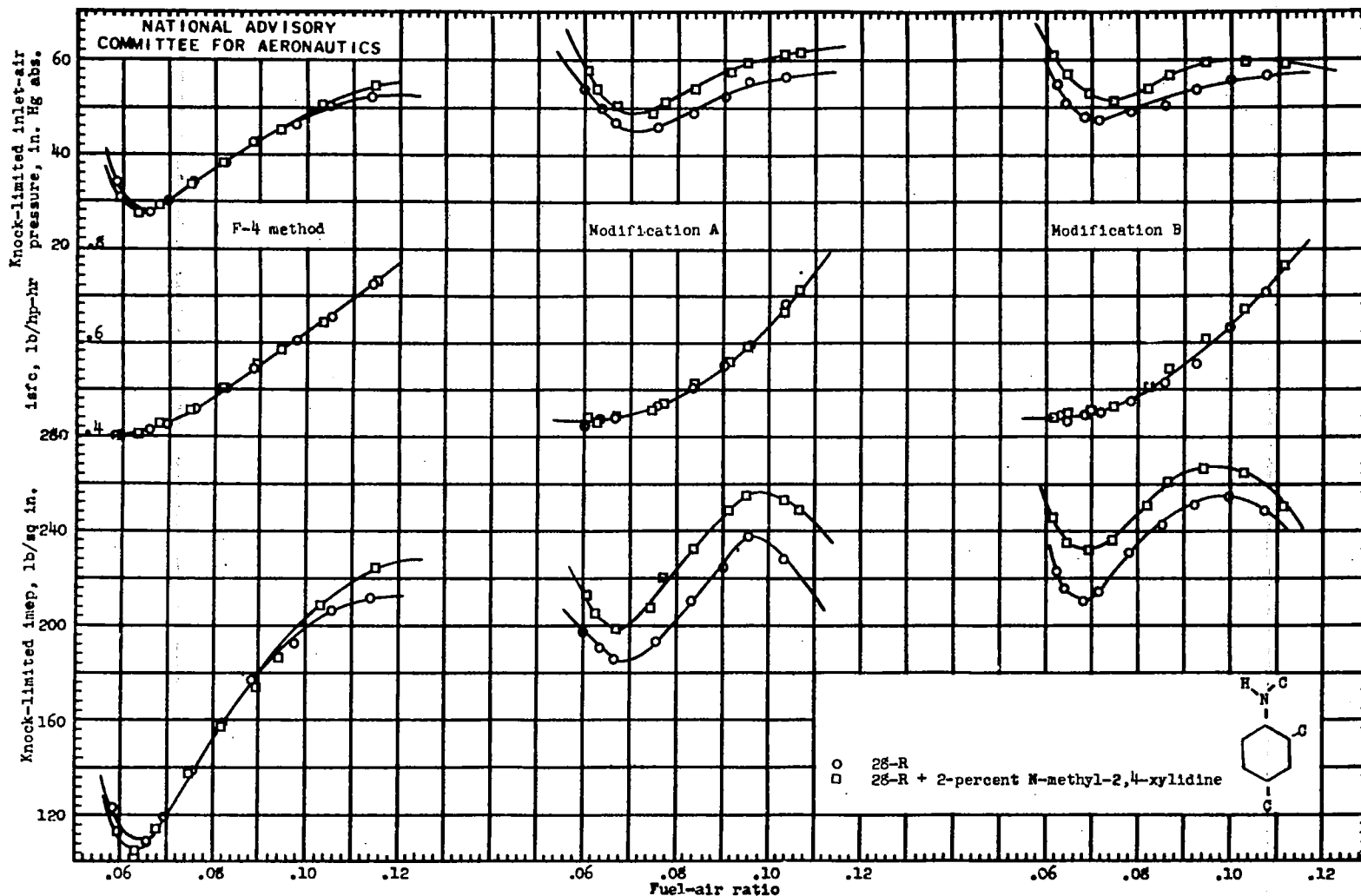


Figure 3. - Effect of addition of 2-percent N-methyl-p-isopropylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.



(a) Inlet-air temperature, 225° F; coolant temperature, 375° F; spark advance, 45° B.T.C.

(b) Inlet-air temperature, 250° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

(c) Inlet-air temperature, 150° F; coolant temperature, 250° F; spark advance, 30° B.T.C.

Figure 4. - Effect of addition of 2-percent N-methyl-2, 4-xylylidine to 28-R fuel on knock-limited performance of a GPR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.

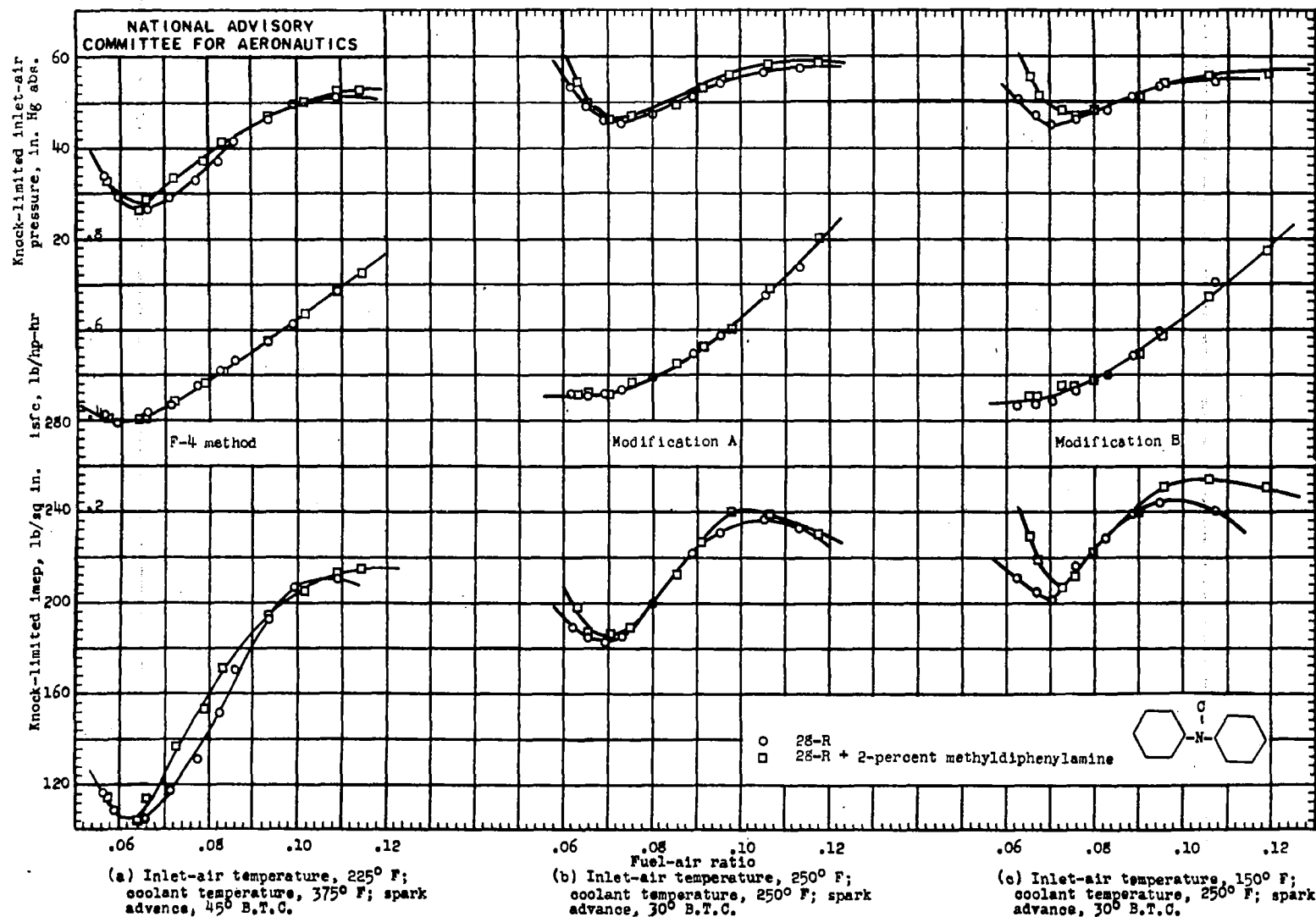


Figure 5. - Effect of addition of 2-percent methyldiphenylamine to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.

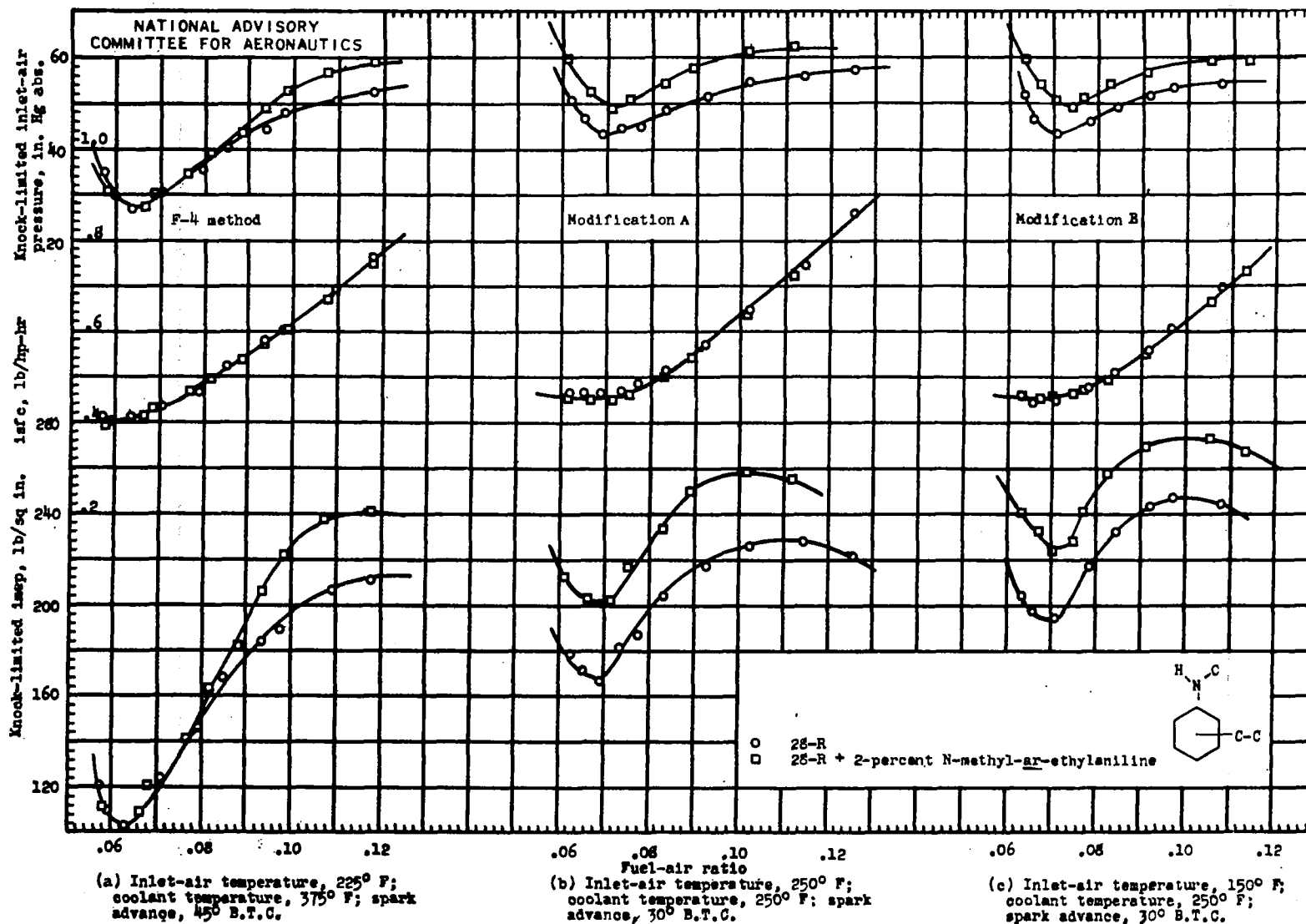


Figure 6. - Effect of addition of 2-percent N-methyl-ar-ethylaniline to 28-R fuel on knock-limited performance of a CFR engine. Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 165° F.

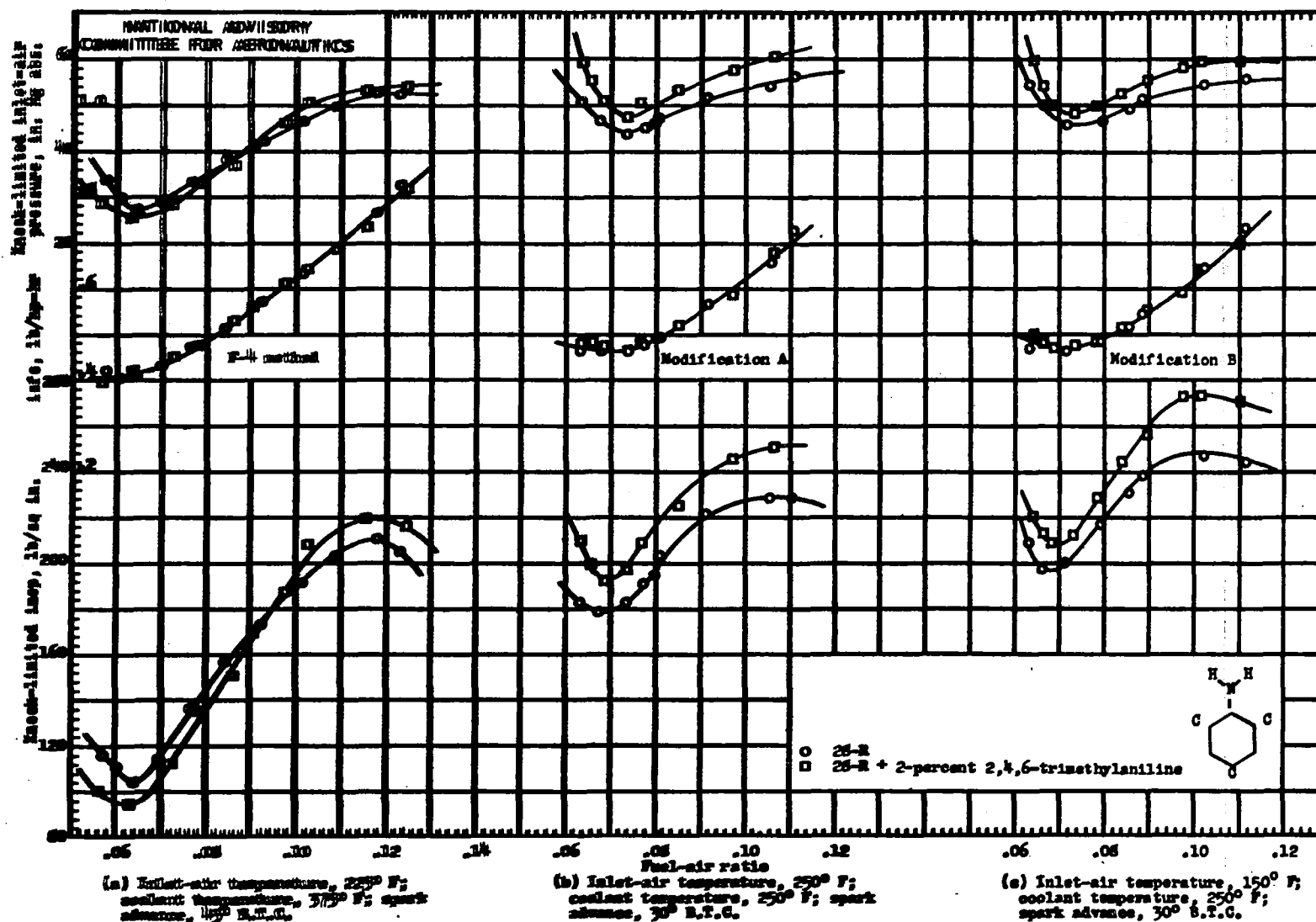


Figure 7. - Effect of addition of 2-percent 2,4,6-trimethylaniline to 28-R fuel on knock-limited performance of a CFR engine.  
Engine speed, 1800 rpm; compression ratio, 7.0; oil temperature, 185° F.

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